SELECTION OF PHASE-CHANGE AND CONTAINMENT MATERIALS FOR THERMAL ENERGY STORAGE

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ABSTRACT

The high thermal conductivity and generally low volume change on melting of germanium and alloys based on silicon make them attractive for storage of thermal energy in space power systems. However, this application obviously depends on identification of suitable container materials that are compatible with these metals at the temperature of interest (>1223 K). An approach to solving the containment problem, involving both chemical and physical compatibility, preparation of NiSi/NiSi$_2$, and initial results for containment of germanium and NiSi/NiSi$_2$ are presented.

INTRODUCTION

Thermal energy storage (TES) systems are required for continuous operation of advanced space power systems using solar energy and Brayton or Stirling heat engines. These storage systems are designed to use the latent heat of fusion of metals or salts. Energy is stored during the heating and melting of a phase change material (PCM) in the sunlit portion of the orbit. The PCM cools and freezes thereby, releasing heat to the engine during the eclipse period of the orbit. Compatibility between phase change materials (PCMs) and containment materials is critical to the viability of these space power systems.

Low density metals are of particular interest as advanced heat storage media because of their high thermal conductivity and generally low volume change on melting as compared to salts. However, the candidate metals are generally reactive with commonly used containment materials, and as a result, the suitable materials are narrowed to ceramics with low connected porosity and small pore size. The compatibility problem for these TES systems was approached from a hierarchy that considers chemical reactivity, solubility, and physical compatibility, especially, thermal expansion mismatch.

MATERIALS

Phase Change Materials

Based on previous work[1] three candidate PCM materials were chosen for the initial screening work. These PCMs were germanium, $NiSi/NiSi_2$ eutectic alloy and Mg_2Si/Si eutectic alloy. Germanium is commercially available. As will be discussed later, the $NiSi/NiSi_2$ eutectic can be readily made, but preparation of Mg_2Si/Si eutectic has presented many unresolved problems.

The appropriate amounts of nickel and silicon for 38 wt% Si were arc melted and homogenized under an argon atmosphere. The molten alloy was drop cast into a water cooled copper mold under under an argon atmosphere. Samples from three different positions along the length of the cast were evaluated using mass spectrometry, X-ray diffraction and metallurgical techniques.

Containment Materials

First, thermochemical analyses were performed to estimate the chemical stability of possible containment materials with molten silicon alloys and germanium at 1100-1300 degrees kelvin. The analyses utilized FACT (Facility for the Analysis of Chemical Thermodynamics, McGill University), and identified Al_2O_3, graphite, silicon carbide, and boron nitride as potential containment materials at the respective melting points of the referenced PCMs.

Secondly, porosity of the containment materials was considered. They should have low porosity and small pore size thereby, limiting the ingress of the molten PCMs into the walls. Ingress of the PCMs can lead to mechanical fatigue of the containment materials from repeated liquid/solid transformation. Graphite with low porosity, chemically vapor deposited (CVD) silicon carbide, and CVD boron nitride meet these criteria. In addition, to minimize the open porosity at the surface that contacts the molten PCMs, the surface of some graphite crucibles were coated with pyrolytically deposited carbon (PyC).

Thirdly, wetting of the container by the molten PCMs was considered. Wetting will aid the ingress of the molten PCMs into the walls of the container with the already mentioned problems, and possible segregation of alloy materials and hence, loss of performance.

Finally, physical compatibility is also an important consideration. The containment materials must have coefficients of thermal expansion and sufficient mechanical strength to accomodate the PCMs' volume changes due to phase transformation and thermal expansion. The thermal expansion coefficients[2] of a few materials with respect to germanium are presented in Figure 1. It should be noted that the expansion of graphite can be varied over a wide range and at least, in theory, be made approximate to that

of germanium. Silicon carbide and boron nitride have expansions less than that of germanium. Thus, a cool down of these materials containing germanium to room temperature can be accomodated. However, a heat up to operating temperature with a solid snug fitting mass of germanium could result in failure of the container.

Alumina was selected as the capsule material for compatibility testing of all materials with silicon alloys (except as noted below), while both graphite and alumina were used to contain germanium. Although it was predicted that graphite would react with the silicon alloys to form silicon carbide, compatibility tests were nevertheless performed to evaluate whether the resultant silicon carbide reaction product would act as a barrier to extensive attack. Alumina, graphite, pyrolytic carbon on graphite, and chemically vapor deposited silicon carbide and boron nitride were obtained from commercial sources.

COMPATIBILITY TESTING

The candidate thermal storage material was placed with the potential container material in an "inert" Al_2O_3 crucible (with cap) or in a crucible (with cap) of the potential container material. The crucible in turn was encapsulated under vacuum (10^{-1} mPa) in quartz. The assembly was heated to 50 degrees K above the melting point of the candidate storage material and maintained at temperature for 168 hours.

Subsequent to exposure, the specimens were subjected to visual, metallographic and scanning electron microscopic analyses.

RESULTS AND DISCUSSION

Characterization of $NiSi/NiSi_2$
Chemical analysis for Ni and Si in the $NiSi/NiSi_2$ alloy was performed via mass spectrometry. Analyses were performed on three specimens taken from either end and the mid-section of the cast specimen and are presented in Table 1. The designations SD1, SD2, and SD3 refer to the top, middle and bottom of the cast specimen respectively. The targeted composition was 38 wt% Silicon. As is shown, there is some variation in composition through the length of casting, and the average silicon content is higher than the targeted concentration. However, the composition is well within the $NiSi/NiSi_2$ two phase field and has a melting point quite close to that of the eutectic.

TABLE 1. Mass Spectrometry of NiSi/NiSi₂ Eutectic Alloy.

| ELEMENT | SPECIMEN ID | | |
	SD1	SD2	SD3
Si wt%	40.9	44.5	42.3
Ni wt%	59.1	55.5	57.7

Optical micrographs of specimen SD4 from the mid-section of the casting are snown in Figures 2 and 3. The specimen was metallographically prepared and etched with 50%HCl/10%Gly/10%HNO₃. A typical eutectic structure is evident with a slight excess of the $NiSi_2$ phase. On comparing Figures 2 and 3, it is seen that the distribution of this excess phase is not uniform and in places is quite small. The cracks suggest severe stress generation during solidification and cooling.

The results of the x-ray diffraction analysis confirm the presence of both the $NiSi_2$ and NiSi phases. Those phases are the ones also indicated by the phase diagram[3]. However, certain features of the x-ray diffraction pattern warrant further discussion. A segment of the diffraction pattern produced using copper k-alpha radiation of wave length 1.54059 Å is shown in Figure 4. The diffraction peaks corresponding to $NiSi_2$ were well defined. The average value of the lattice parameter calculated from the identified lattice planes is 5.396 ± 0.008 Å. In fact the (333) and (440) reflections gave a lattice parameter of 5.400 Å. That is to be compared to 5.406 Å for $NiSi_2$ (48.90 wt% Si)[3] with a CaF_2 (C1) type structure. The remaining diffraction peaks were quite broad. This broadening renders the analysis more difficult and more ambiguous. In this case the lattice parameter values of NiSi (32.37 wt% Si)[3] with an orthorhombic structure of a = 5.62 Å, b = 5.18 Å, c = 3.34 Å were used to back calculate the diffraction angles. Comparisons were made versus the broad peak positions. There was good agreement between the centroids of the broad peaks and the calculated diffraction angles. The broadening could be a result of stresses generated during casting of this material and/or a range of stoichiometry for NiSi. The latter is not indicated in the phase diagram[3]. As a result of the aforementioned broadening, the possible presence of third phase could not be absolutely ruled out.

Compatibility Studies with Germanium
The short term exposures (168 hours, 1283 K) of germanium to graphite, PyC, silicon carbide and CVD boron nitride all indicated good compatibility. There were no detectible chemical reactions and no migration of the germanium into the test

containment materials. There was adequate physical compatibility as all the capsules remained intact on cooling to room temperature. However, as presented in the companion paper[4], depending on the grade of graphite, there can be seepage of germanium through the walls during thermal cycling.

Compatibility Studies with $NiSi/NiSi_2$ Eutectic Alloy

A similar exposure of $NiSi/NiSi_2$ eutectic alloy to pyrolytic carbon on graphite, alumina, CVD silicon carbide in an alumina crucible and CVD boron nitride in an alumina crucible was performed at 1289 K. In all cases, on completion of the experiments, it was found that the crucibles had broken. However, the $NiSi/NiSi_2$ ingot was totally retained within the crucible and appeared to have solidified with the crucible still in tact. This would indicate that the crucible broke on cooling. Neither the coefficient of thermal expansion nor the volume change (expansion) on freezing of $NiSi/NiSi_2$ is known at this time. Therefore, it can only be speculated as to whether failure occurred at the liquid to solid transformation or after further cooling. Initial metallographic results of this short term isothermal screening for pyrolytic carbon, CVD silicon carbide and CVD boron nitride appear favorable from a chemical compatibility perspective.

An optical micrograph of $NiSi-NiSi_2$ tested at 1289 K for 168 hours, in a crucible of pyrolytic carbon of thickness 0.005 cm (0.0020 inches) on graphite is shown in Figure 5. Note that there is a very thin layer of the pyrolytic carbon attached to the alloy with little evidence of reaction for this isothermal short term experiment.

An SEM micrograph of a portion of the pyrolytic carbon on graphite near a fracture site of the crucible is shown in Figure 6. This surface was in contact with molten $NiSi-NiSi_2$ at temperature. Note there are indications that the pyrolytic carbon has been pulled away from part of the graphite surface. EDX analysis indicated that there was more nickel and silicon on the pyrolytic carbon surface than on the graphite surface. However this analysis is complicated by the presence of "foreign" elements such as Al, Fe, Ca, and Si in the graphite.

A negative meniscus was observed with CVD silicon carbide indicating a non-wetting system. A scanning electron microscope energy dispersive examination of the $NiSi-NiSi_2/SiC$ interface indicated that one small area of the chemical vapor deposited SiC was wetted by the $NiSi-NiSi_2$ eutectic alloy at the test temperature. This specimen was sectioned and the area of interest prepared for metallographic examination. At present, nothing unique has been observed in that area. Also, the energy dispersive analysis indicated that there was a small amount of Al on the surrounding surface of the $NiSi-NiSi_2$ alloy. The quantity is quite small and appears to be a dusting of Al_2O_3.

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SUMMARY

The compatibility of containment materials with metal based PCM was approached by considering chemical reactivity, solubility, and physical compatibility, especially, thermal expansion mismatch.

Thermodynamics indicate that carbon (graphite) should be a good containment material for germanium. This was confirmed experimentally under short term isothermal conditions. Confirmation under cyclic conditions, as presented in the companion paper[*], has been demonstrated. Germanium contained within graphite has proven to be a viable TES system. The initial phase of this work has also demonstrated that germanium is compatibile with pyrolytic carbon, CVD silicon carbide, and CVD boron nitride.

It has been demonstrated that $NiSi/NiSi_2$ can be readily produced and qualified. There appears to be a minor reaction between $NiSi/NiSi_2$ and pyrolytic carbon. However, the long term effect of this reaction needs further investigation. CVD silicon carbide and CVD boron nitride also appear promising for containment of $NiSi/NiSi_2$ from a chemical compatibility view.

DISCLAIMER

REFERENCES

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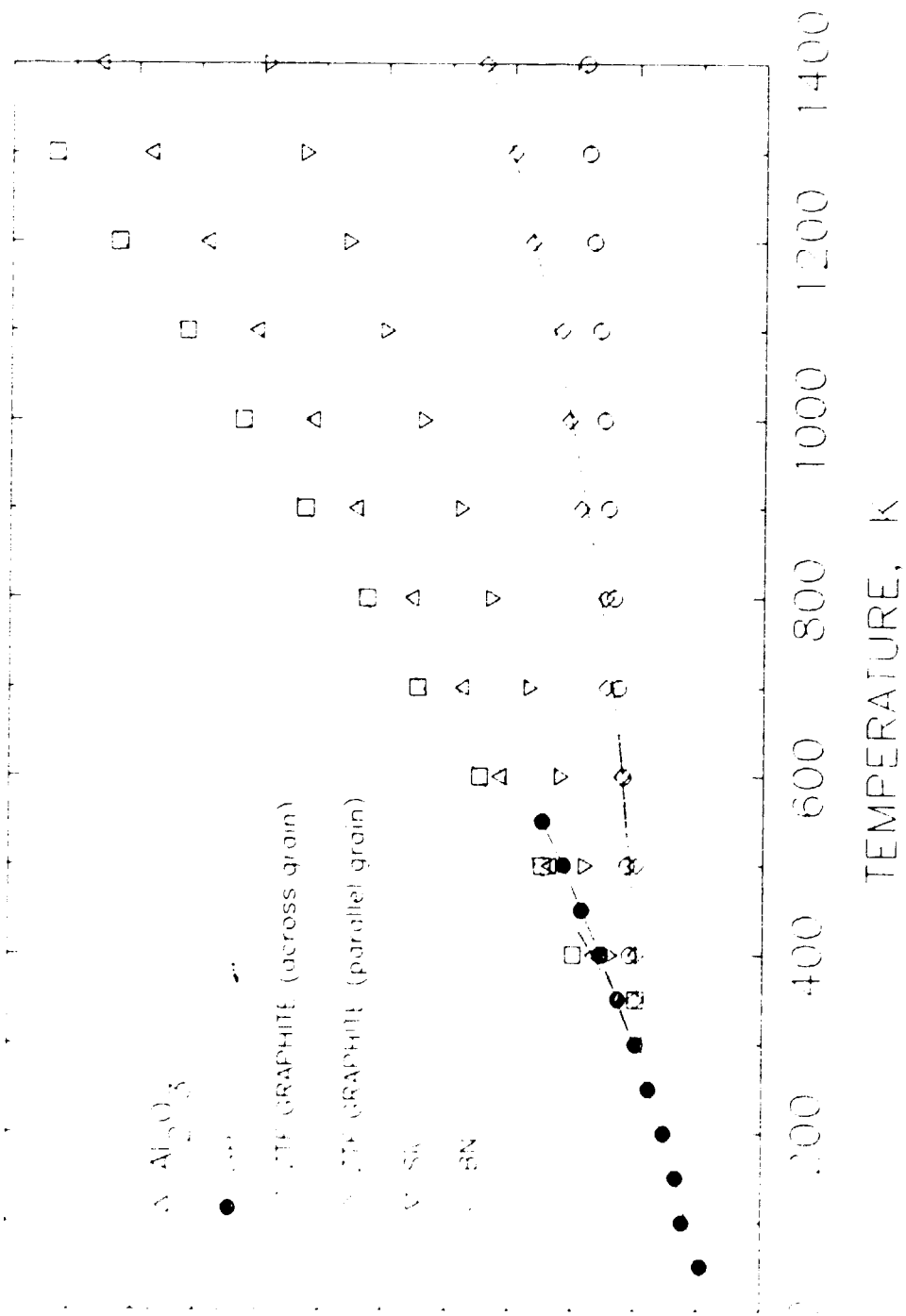
Figure 1. Thermal expansion coefficients of germanium and select containment materials[2].

100 μm   200x

Figure 2. Optical micrograph of NiSi-NiSi$_2$ specimen SD4, etched with 50%HCl/10%Gly/10%HNO$_3$.

100 μm   200X
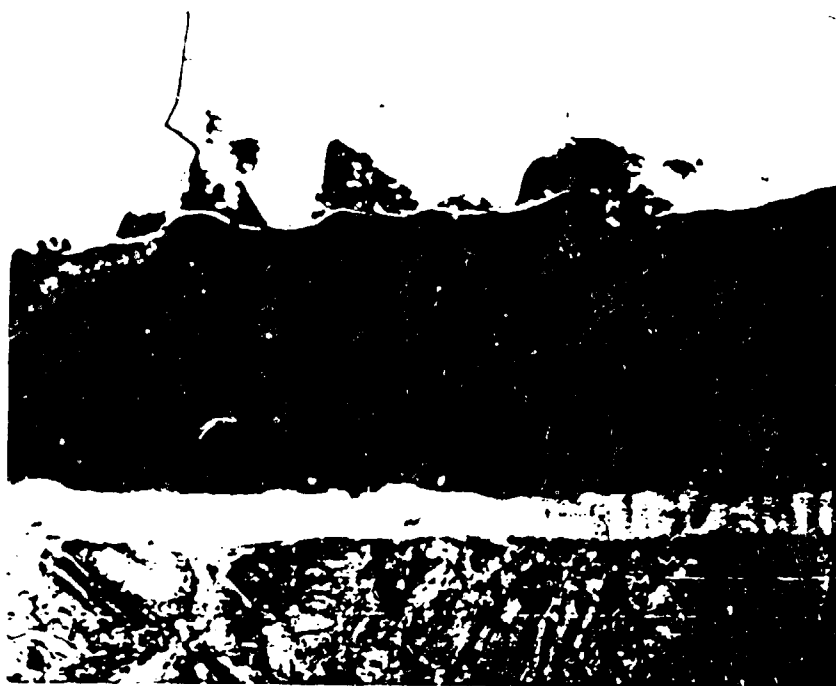
Figure 3. Optical micrograph of NiSi-NiSi₂ specimen SD4, etched with
50%HCl/10%Gly/10%HNO₃. As compared to Figure 2, there is a small
quantity of an excess phase.

Figure 4. Segment of x-ray diffraction pattern of NiSi-NiSi$_2$ eutectic, using copper k-alpha radiation of wavelength 1.54059 Å.

FN:CT386C.NI   ID:SAMPLE DWSD5, NI-SI EUTECTIC, WILSO SCINTAG/USA
DATE: 4/ 6/88   TIME:15:56   PT: 6.000 STEP: .020   WL:1.54059

FULL-COPY PCOPY PAGE TITLE CYCLE ⊃ ANGLE END OVERLAP REPOS CURSOR LABEL
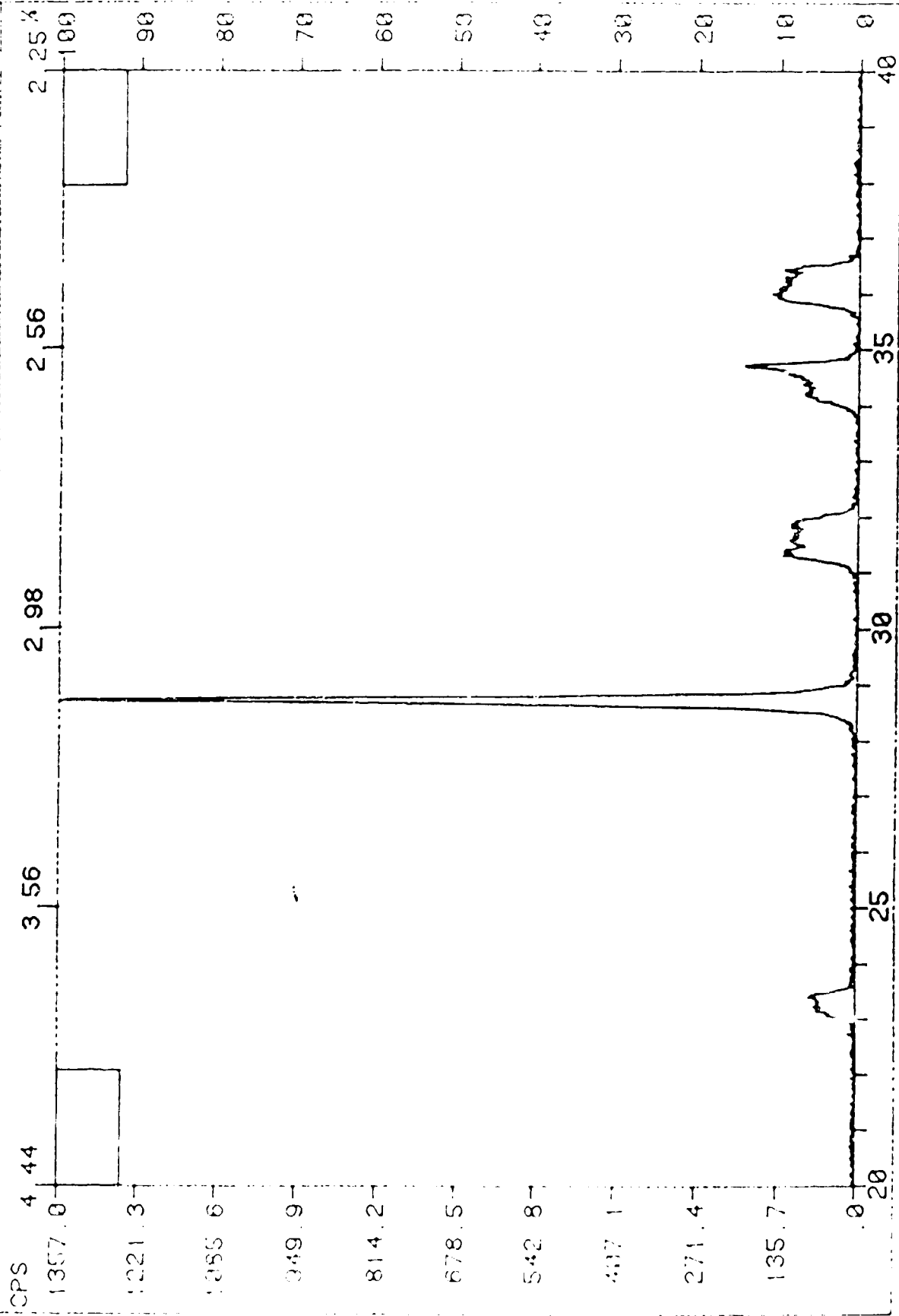
Figure 5. Optical micrograph of NiSi-NiSi$_2$ reacted at 1289 K, for 168 hours, in a crucible of pyrolytic carbon of thickness 0.005 cm (0.0020 inches) on graphite. Magnification is 400X.

Note that there is a very thin layer of the pyrolytic carbon attached to the alloy. Suggesting a minor reaction for this isothermal short term experiment.
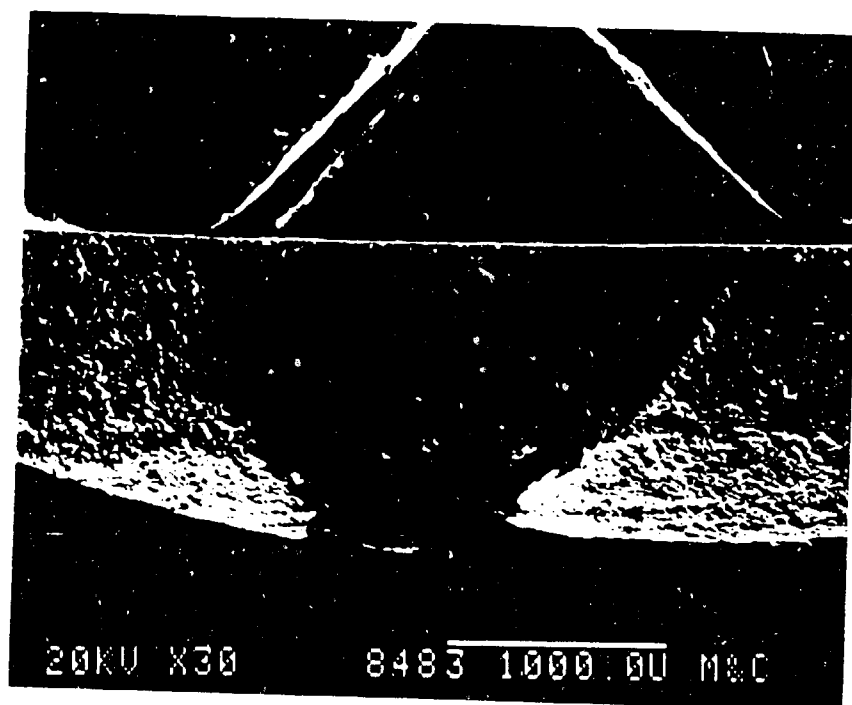
Figure 6. SEM micrograph of a portion of the pyrolytic carbon on graphite near fracture site of crucible. This surface was in contact with molten NiSi-NiSi$_2$ at temperature.

Note there are indications that the pyrolytic carbon has been pulled away from part of this surface.